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## EUROPEAN PATENT APPLICATION

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(54) Chemically crosslinked ultrahigh molecular weight polyethylene for artificial human joints

(57) The present invention discloses a method for enhancing the wear-resistance of polymers by crosslinking them, especially before irradiation steriliza-

tion. In particular, this invention presents the use of chemically crosslinked ultrahigh molecular weight polyethylene in in vivo implants.

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On the other hand, it has been reported that the best total hip prosthesis for withstanding wear is one with an alumina head and an irradiated UHMW polyethylene socket, as compared to a un-irradiated socket. The irradiated socket had been irradiated with  $10^8$  rad of  $\gamma$ -radiation, or about 40 times the usual sterilization dose. (Oonishi, H., et al., Radiat. Phys. Chem., **39**(6):495-504 (1992)). The usual average sterilization dose ranges from 2.5 to 4.0 Mrad. Other investigators did not find any significant reduction in the wear rates of UHMW polyethylene acetabular cups which had been irradiated, in the solid phase, in special atmospheres to reduce oxidation and encourage crosslinking. (Ferris, B.D., J. Exp. Path., **71**:367-373 (1990); Kurth, M., et al., Trans. Third World Biomaterials Congress, 589 (1988); Roe, R.J., et al., J. Biomed. Materials Res., **15**:209-230 (1981); Rose, et al., J. Bone & Joint Surgery, **62A**(4):537-549 (1980); Streicher, R.M., Plastics & Rubber Processing & Applications, **10**:221-229 (1988)).

Meanwhile, DePuy/DuPont Orthopaedic has fabricated acetabular cups from conventionally extruded bar stock that has previously been subjected to heating and hydrostatic pressure that reduces fusion defects and increases the crystallinity, density, stiffness, hardness, yield strength, and resistance to creep, oxidation and fatigue. (U.S. Patent No. 5,037,928, to Li, et al., Aug. 6, 1991; Huang, D. D. & Li, S., Trans. 38th Ann. Mtg., Orthop. Res. Soc., **17**:403 (1992); Li, S. & Howard, E. G., Trans. 16th Ann. Society for Biomaterials Meeting, Charleston, S.C., 190 (1990).) Silane cross-linked UHMW polyethylene (XLP) has also been used to make acetabular cups for total hip replacements in goats. In this case, the number of *in vivo* debris particles appeared to be greater for XLP than conventional UHMW polyethylene cup implants (Ferris, B. D., J. Exp. Path., **71**:367-373 (1990)).

Other modifications of UHMW polyethylene have included: (a) reinforcement with carbon fibers ("Poly Two Carbon-Polyethylene Composite-A Carbon Fiber Reinforced Molded Ultra-High Molecular Weight Polyethylene", Technical Report, Zimmer (a Bristol-Myers Squibb Company), Warsaw (1977)); and (b) post processing treatments such as solid phase compression molding (Eyerer, P., Polyethylene, Concise Encyclopedia of Medical & Dental Implant Materials, Pergamon Press, Oxford, 271-280 (1990); Li, S., et al., Trans. 16th Annual Society for Biomaterials Meeting, Charleston, S.C., 190 (1990); Seedhom, B.B., et al., Wear, **24**:35-51 (1973); Zachariades, A.E., Trans. Fourth World Biomaterials Congress, 623 (1992)). However, to date, none of these modifications has been demonstrated to provide a significant reduction in the wear rates of acetabular cups. Indeed, carbon fiber reinforced polyethylene and a heat-pressed polyethylene have shown relatively poor wear resistance when used as the tibial components of total knee prosthesis. (Bartel, D.L., et al., J. Bone & Joint Surgery, **68-A**(7):1041-1051 (1986); Connelly, G.M., et al., J. Orthop. Res., **2**:119-125 (1984); Wright, T.M., et al., J. Biomed. Materials Res., **15**: 719-730 (1981); Bloebaum, R.D., et al., Clin. Orthop., **269**:120-127 (1991); Goodman, S. & Lidgren, L., Acta orthop. Scand., **63**(3) 358-364 (1992); Landy, M. M. & Walker, P.S., J. Arthroplasty, Supplement, **3**:S73-S85 (1988); Rimnac, C.M., et al., Trans. Orthopaedic Research Society, **17**:330 (1992); Rimnac, C.M. et al., "Chemical and mechanical degradation of UHMW polyethylene: Preliminary report of an *in vitro* investigation," ASTM Symposium on Biomaterials' Mechanical Properties, Pittsburgh, May 5-6 (1992)).

### Summary Of The Invention

One aspect of the invention presents a method for reducing the crystallinity of a polymer so that it can better withstand wear. An effective method for reducing the crystallinity of the polymer is by crosslinking. For reduction of crystallinity, the polymer may be irradiated in the melt or, preferably, chemically crosslinked in the molten state. The method is particularly useful for polymer which undergoes irradiation sterilization in the solid state. It is advantageous if the crosslinked polymer is annealed to stabilize its shrinkage.

Another aspect of the invention presents a method for making *in vivo* implants based on the above treatment of the polymer.

Another aspect of the invention presents a polymer, made from the above method, having an increased ability to withstand wear.

Another aspect of the invention presents *in vivo* implants made from the polymer described above.

### Brief Description Of The Drawings

FIG. 1 presents SEM micrographs of fracture surfaces of the compression molded UHMW polyethylene (after irradiation) at magnifications of (A) x 200 and (B) x 5000.

FIG. 2 presents SEM micrographs of fracture surfaces of compression molded UHMW polyethylene crosslinked with 1 wt% peroxide (after irradiation) at magnifications of (A) x 200 and (B) x 5000.

FIG. 3 presents the geometry of the acetabular cup tested for wear on the hip joint simulator used in EXAMPLE 2 below.

FIG. 4 presents a schematic diagram of the hip joint simulator used in EXAMPLE 2 below.

FIG. 5 presents a graph comparing the amounts of wear of the modified and unmodified UHMW polyethylene cups during a run lasting a million cycles.

25% in crystallinity compared to the originally uncrosslinked but radiation sterilized UHMW polyethylene which possessed about 55.8% crystallinity. Thus, it is contemplated that after the usual sterilization dosage in the solid state, which generally averages between 2.5 to 4.0 Mrad, the treated polymer preferably possesses less than about 45% crystallinity, and more preferably about 42% crystallinity or less. Also, the treated polymer preferably possesses less than about 43%, more preferably less than about 40%, crystallinity before irradiation in the solid state.

If the polymer is to be molded, e.g. as an acetabular cup, the polymer may be placed in the mold and crosslinked therein. Further crosslinking examples are: (1) irradiation of the polymer when it is in a molten state, e.g. UHMW polyethylene has been crosslinked in the melt by electron beam irradiation; and molten linear polyethylene has been irradiated with fast electrons (Dijkstra, D.J. et al., Polymer, 30:866-709 (1989); Gielenz G. & Jungnickle, B.J., Colloid & Polymer Sci., 260:742-753 (1982)); the polymer may also be gamma-irradiated in the melt; and (2) photocrosslinking of the polymer in the melt, e.g. polyethylene and low-density polyethylene have been photocrosslinked (Chen, Y.L. & Ranby, B., J. Polymer Sci.: Part A: Polymer Chemistry, 27:4051-4075, 4077-4086 (1989)); Qu, B.J. & Ranby, B., J. Applied Polymer Sci., 48:711-719 (1993)).

### Choices of Polymers

The polymers are generally polyhydrocarbons. Ductile polymers that wear well are preferred. Examples of such polymers include: polyethylene, polypropylene, polyester and polycarbonates. For example, UHMW polymers may be used, such as UHMW polyethylene and UHMW polypropylene. An UHMW polymer is a polymer having a molecular weight (MW) of at least about a million.

For *in vivo* implants, the preferred polymers are those that are wear resistant and have exceptional chemical resistance. UHMW polyethylene is the most preferred polymer as it is known for these properties and is currently widely used to make acetabular cups for total hip prostheses. Examples of UHMW polyethylene are: Hostalen GUR 415 medical grade UHMW polyethylene flake (Hoechst-Celanese Corporation, League City, Texas), with a weight average molecular weight of  $6 \times 10^6$  MW; Hostalen GUR 412 with a weight average molecular weight of between  $2.5 \times 10^6$  to  $3 \times 10^6$  MW; Hostalen GUR 413 of  $3 \times 10^6$  to  $4 \times 10^6$  MW; RCH 1000 (Hoechst-Celanese Corp.); and HiFax 1900 of  $4 \times 10^6$  MW (HiMont, Elkton, Maryland). GUR 412, 413 and 415 are in the form of powder. RCH 1000 is usually available as compression molded bars. Historically, companies which make implants have used GUR 412 and GUR 415 for making acetabular cups. Recently, Hoechst-Celanese Corp. changed the designation of GUR 415 to 4150 resin and indicated that 4150 HP was for use in medical implants.

### Methods for Characterizing the Polymers (Especially the Determination of Their Crystallinity)

The degree of crystallinity of the crosslinked polymer may be determined after it has been crosslinked or molded. In case the treated polymer is further irradiated, e.g., to sterilize the polymer before its implant into humans, the degree of crystallinity may be determined after irradiation, since irradiation effects further crystallization of the polymer.

The degree of crystallinity can be determined using methods known in the art, e.g. by differential scanning calorimetry (DSC), which is generally used to assess the crystallinity and melting behavior of a polymer. Wang, X. & Salovey, R., J. App. Polymer Sci., 34: 593-599 (1987).

X-ray scattering from the resulting polymer can also be used to further confirm the degree of crystallinity of the polymer, e.g. as described in Spruiell, J.E., & Clark, E.S., in "Methods of Experimental Physics", L. Marton & C. Marton, Eds., Vol. 16, Part B, Academic Press, New York (1980). Swelling is generally used to characterize crosslink distributions in polymers, the procedure is described in Ding, Z. Y., et al., J. Polymer Sci., Polymer Chem., 29: 1035-38 (1990). Another method for determining the degree of crystallinity of the resulting polymer may include FTIR (Painter, P.C. et al., "The Theory Of Vibrational Spectroscopy And Its Application To Polymeric Materials", John Wiley and Sons, New York, U.S.A. (1982)) and electron diffraction. FTIR assesses the depth profiles of oxidation as well as other chemical changes such as unsaturation (Nagy, E.V., & Li, S., "A Fourier transform infrared technique for the evaluation of polyethylene orthopaedic bearing materials", Trans. Soc. for Biomaterials, 13:109 (1990); Shinde, A. & Salovey, R., J. Polymer Sci., Polym. Phys. Ed., 23:1681-1689 (1985)). A further method for determining the degree of crystallinity of the resulting polymer may include density measurement according to ASTM D1505-68.

### Methods for Chemically Crosslinking the Polymers

The polymer is preferably chemically crosslinked to decrease its crystallinity. Preferably, the crosslinking chemical, i.e. a free radical generating chemical, has a long half-life at the molding temperature of the chosen polymer. The molding temperature is the temperature at which the polymer is molded. The molding temperature is generally at or above the melting temperature of polymer. If the crosslinking chemical has a long half-life at the molding temperature, it will decompose slowly, and the resulting free radicals can diffuse in the polymer to form a homogeneous crosslinked

Use of Crosslinked Polymers for In Vivo Implants

Another aspect of the invention presents a process for making in vivo implants using the above chemically crosslinked polymer. Since in vivo implants are often irradiated to sterilize them before implant, the present invention provides the further step of selecting for implant use, a polymer with about 45% crystallinity or less after irradiation sterilization. For  $\gamma$ -irradiation sterilization, the minimum dosage is generally 2.5 Mrad. The sterilization dosage generally falls between 2.5 and 4.0 Mrad. The preferable degree of crystallinity is between 25% to 45% crystallinity. In EXAMPLE 2 below, the polymer has about 39.8% crystallinity after crosslinking; and about 42% crystallinity after further irradiation with  $\gamma$ -radiation to an average dose of about 3.4 Mrad. Thus, the chemically crosslinked UHMW polymer preferably possesses less than about 43% crystallinity before irradiation in the solid state, and less than about 45% crystallinity after irradiation with  $\gamma$ -radiation to an average dose of about 3.4 Mrad.

Annealing of Crosslinked Polymers

Applicants observed that both crosslinked and uncrosslinked polymers tended to shrink, but the crosslinked polymer tended to shrink more than the uncrosslinked polymer (see EXAMPLE 3 below). Thus, the present invention further provides for annealing a polymer to pre-shrink it to a size which will not shrink further (i.e. stabilize the polymer's shrinkage or size). Thus, one aspect of the invention provides for a method of: 1) crosslinking a polymer, 2) selecting a crosslinked polymer of reduced crystallinity, 3) annealing the polymer to stabilize its size. Thus, the polymer can be molded at a size larger than desired, and the molded polymer is then annealed to stabilize its size. After size stabilization, the molded polymer is then resized, such as by machining, into a product with the desired dimension.

The annealing temperature is preferably chosen to avoid thermal oxidation of the crosslinked polymer which will increase its crystallinity. Thus, the annealing temperature is preferably below the melting point of the molded polymer before irradiation. For example, the melting temperatures of molded UHMW polyethylene and molded 1 wt% peroxide UHMW polyethylene are 132.6°C and 122.3°C, before irradiation, respectively. The preferable annealing temperature for both these molded UHMW polyethylenes is between 60°C to 120°C, before irradiation, and more preferably 100°C. These temperatures were determined by observation, based on experiments, of their minimal effect on thermal oxidation of the molded polymers. The annealing time is generally between 1 to 6 hours, and more preferably between 2 to 4 hours. In the case of UHMW polyethylene, the annealing time is preferably between 2 to 4 hours, and more preferably about 2 hours.

To further avoid thermal oxidation of the crosslinked polymer, the annealing is most preferably conducted in a vacuum oven.

To ensure that the crosslinked and annealed polymer has the desired degree of crystallinity, its degree of crystallinity is preferably determined after the annealing process, using the method(s) described previously.

Wear-Resistant Polymers

Another aspect of the invention presents a polymer with 45% of crystallinity or less, in particular, after irradiation in the solid state and/or annealing. In EXAMPLE 2 below, the polymer has about 39.8% crystallinity after crosslinking; and about 42% crystallinity, after further irradiation with  $\gamma$ -radiation to an average dose of about 3.4 Mrad; or about 40.8% crystallinity, after crosslinking and annealing, but before irradiation in the solid state.

The polymers of the present invention can be used in any situation where a polymer, especially UHMW polyethylene, is called for, but especially in situations where high wear resistance is desired and irradiation of the solid polymer is called for. More particularly, these polymers are useful for making in vivo implants.

In Vivo Implants Made of Crosslinked Polymers

An important aspect of this invention presents in vivo implants that are made with the above polymers or according to the method presented herein. These implants are more wear resistant than their untreated counterpart, especially after irradiation. In particular, these in vivo implants are chemically crosslinked UHMW polymers, which have been molded, annealed, and resized into the shape of the implants. Further, the chemically crosslinked UHMW polymer preferably possesses less than about 43% crystallinity before irradiation in the solid state, and less than about 45% crystallinity, after  $\gamma$ -irradiation to an average dose of 3.4 Mrad, in the solid state. The modified polymer can be used to make in vivo implants for various parts of the body, such as components of a joint in the body. For example, in the hip joints, the modified polymer can be used to make the acetabular cup, or the insert or liner of the cup, or trunnion bearings (e.g. between the modular head and the stem). In the knee joint, the modified polymer can be used to make the tibial plateau (femoro-tibial articulation), the patellar button (patello-femoral articulation), and trunnion or other bearing components, depending on the design of the artificial knee joint. In the ankle joint, the modified polymer can

B26:37 (1957); Bhateja, S.K., *J. Macromol. Sci. Phys.*, B22:159 (1983); Bhateja, S.K., et al., *J. Polym. Sci., Polym. Phys. Ed.*, 21:523 (1983); Kamel, I. & Finegold, L., *J. Polym. Sci., Polym. Phys. Ed.*, 23:2407 (1985); Shinde, A. & Salovey, R., *J. Polym. Sci., Polym. Phys. Ed.*, 23:1681 (1985); Bhateja, S.K. & Andrews, E.H., *J. Mater. Sci.*, 20:2839 (1985); Minkova, L., *Colloid Polym. Sci.*, 266:6 (1988); Minkova, L. & Mihailov, M., *Colloid Polym. Sci.*, 268:1018 (1990) and Zhao, Y., et al., *J. Appl. Polym. Sci.*, 50:1797 (1993)). The gel content after irradiation for the peroxide-free specimen was 70.8%.

For the 1 wt% peroxide specimen, the degree of crystallinity and peak melting temperature after irradiation were increased to 42% (about 2% increase) and 125.1°C, respectively. The gel content decreased to 97.5% after irradiation, whereas, the degree of swelling and molecular weight between crosslinks increased to 3.35 and 2782 (g/mol), respectively. Apparently, irradiation-induced scission of taut tie molecules resulted in a decreased gel content and an increased degree of swelling. However, after peroxide crosslinking, the effect of irradiation on network properties was mitigated. As a result of peroxide crosslinking, radiation-induced chain scission becomes less important in determining gel content. We suggest that peroxide crosslinking reduces the effect of irradiation on the crosslinked network because crosslinks introduced by peroxide crosslinking stabilize chain fragments resulting from the scission of taut tie molecules and suppress recrystallization of broken chains. Wide-angle x-ray scattering showed that crystal perfection increased after irradiation. It is suggested that crystal perfection was improved by irradiation-induced scission of taut tie molecules in the amorphous regions.

FTIR measurements showed that, after irradiation, the carbonyl concentration significantly increased. This is because the free radicals produced by irradiation reacted with oxygen dissolved and/or diffused in the polymer. In addition, the carbonyl concentration in irradiated peroxide-crosslinked samples was higher, compared to the peroxide-free sample (after irradiation). Peroxide crosslinking produces tertiary carbons, therefore, the concentration of tertiary carbons increases with increasing peroxide concentration. Applicants believe that tertiary carbons are more susceptible to oxidation during irradiation. Therefore, carbonyl concentration in the irradiated peroxide-crosslinked samples increased with increasing peroxide concentration.

After irradiation, scanning electron micrographs were taken of the fracture surfaces of the peroxide-free and 1 wt% peroxide specimens, compression molded at 170°C for 2 hours and subsequently slowly cooled to room temperature. The micrographs are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, a brittle (rough) fracture boundary of size comparable to that of the original UHMW polyethylene powder particles is observed. Close examination (x 5000 magnification) shows an oriented nodular structure, composed of many smooth, submicron spheres. These smooth, minute spheres are believed to correspond to those present in the raw UHMW polyethylene powder and to form an aggregate. In Fig. 2, peroxide crosslinked samples show a ductile (smooth) fracture surface, compared to the rough fracture surface of peroxide-free specimen. The difference in appearance of fracture surfaces for peroxide-free and 1 wt% peroxide specimens is due to the crystallinity difference. After irradiation, the degree of crystallinity for the peroxide-free and 1 wt% peroxide specimens were 55.8 and 42%, respectively. It is believed that the peroxide-free specimen (55.8% crystallinity) suffered higher forces and less deformation during the fracturing process, leading to a sharp break in the polymer.

The crosslinking experiment was also conducted with different concentrations of Lupersol 130, using a smaller amount, 5 g, of GUR 415 and a smaller mold which was in the form of a disk. It was observed that the degree of crystallinity of the crosslinked polymer decreased with increased concentrations of Lupersol 130. The result is shown in Table 1 below:

TABLE 1

wt% Peroxide	Crystallinity (%) Before Irradiation	Crystallinity (%) After Irradiation
0	49.2	55.8
0.2	44.0	50.0
0.4	41.6	46.8
0.6	41.3	46.2
0.8	40.0	45.0
1.0	39.8	42.0
1.5	36.8	36.8
2.0	36.5	36.7

and compared for all of the cups only for the interval from 0.5 to 1.0 million cycles. The four control polyethylene cups showed comparable amounts of wear (Fig. 5), with an average corrected wear rate of 19.19 (S.D.=2.38) milligrams per million cycles (Table 2). This was within the range that applicants have measured for cups of conventional UHMW polyethylene in a variety of studies that applicants have run.

The wear was much lower for the modified cups (Fig. 5). As shown in Table 2, the mean wear rate for the modified cups was 4.12 (S.D.=1.26) milligrams per million cycles, i.e. about one-fifth of the wear of the control cups. This difference was statistically significant at the level of  $p=0.0002$ .

TABLE 2

WEAR RATES FOR CONTROL AND MODIFIED POLYETHYLENES (INTERVAL FROM 0.5 TO 1.0 MILLION CYCLES)			
MATERIAL	CUP NUMBER	WEAR RATE (mg/million cycles)	MEAN WEAR RATE (STANDARD DEVIATION)
CONTROL POLYETHYLENE	C2	21.67	19.19 (2.38)
	C3	16.78	
	C4	17.57	
	C9	20.76	
MODIFIED POLYETHYLENE	M4	4.08	4.12 (1.26)
	M5	2.88	
	M7	5.39	

For the data point at 0.5 million cycles, the corrected weights were lower than the weights before the wear test. This was most likely the result of the wear being very small, and the fluid absorption by the test cups being slightly greater than the average gain of the soak correction cups, such that the correction factor did not entirely offset the fluid gain by the wear cups (giving an apparent "negative" wear). A small difference in water absorption rates between the wear cups and the correction cups could arise due to differences in equilibrium temperatures (the wear cups were typically at 35°C to 45°C, whereas the soak correction cups were at room temperature, about 20°C), due to mechanical agitation of the serum during oscillation of the wear test chambers, or other causes.

### EXAMPLE 3

During the wear test in the simulator described in EXAMPLE 2, it was discovered that the acetabular cups shrunk at simulated human body temperature. In order to stabilize the shrinkage, in this experiment (unrelated to EXAMPLE 2), the cups were annealed at 100°C in a vacuum oven for 2 hours. After annealing, the total shrinkage in diameter for uncrosslinked and crosslinked cups was approximately 1% and 2%, respectively. The degrees of crystallinity of the annealed cups were determined by DSC. The degree of crystallinity of the uncrosslinked polymer was unchanged, whereas that of the crosslinked polymer was increased by approximately 1%. To test for further shrinkage, the cups were again put in the vacuum oven at 80°C for two hours, and no further shrinkage was observed.

The present invention has been described with reference to specific embodiments. However, this application is intended to cover those changes and substitutions which may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

### Claims

1. A method for producing a crosslinked polymer with increased ability to withstand wear, comprising the steps of:
  - a) crosslinking a polymer to form a crosslinked polymer;
  - b) determining the degree of crystallinity of the crosslinked polymer; and
  - c) adjusting reaction conditions such that the degree of crystallinity of the polymer after crosslinking is reduced by 10% to 50%;
 wherein the crosslinking is achieved by a method selected from the group consisting of:
  - i) irradiation crosslinking of the polymer when it is in a molten state;

16. An in vivo implant made by a polymer produced by the method comprising the steps of:

- a) reducing the crystallinity of the polymer to enable it to better withstand wear; and
- b) molding the polymer into a shape suitable for in vivo implant;

wherein the reduction of crystallinity in step (a) does not include irradiating the polymer in a solid state.

17. The in vivo implant of claim 16, wherein the step (a) is achieved by crosslinking the polymer using a method selected from the group consisting of:

- a) irradiation crosslinking of the polymer when it is in a molten state;
- b) photocrosslinking of the polymer in the melt; and
- c) crosslinking of the polymer with a free radical generating chemical.

18. The in vivo implant of claim 17, wherein the polymer is chemically crosslinked with a free radical generating chemical.

19. The in vivo implant of claim 18, wherein the free radical generating chemical is selected from the group consisting of: peroxides, peresters, azo compounds, disulfides, dimethacrylates, tetrazenes, and divinyl benzene.

20. The in vivo implant of claim 19, wherein the crosslinking reduces the crystallinity of the polymer by 10 to 50%.

21. The in vivo implant of claim 20, wherein the polymer is a polyhydrocarbon.

22. The in vivo implant of claim 21, wherein the polyhydrocarbon is an UHMW polyhydrocarbon.

23. The in vivo implant of claim 17, wherein the in vivo implant is capable of possessing about 45% crystallinity or less if irradiated by gamma irradiation to an average dose of about 3.4 Mrad or less.

24. The in vivo implant of claim 23, wherein the polymer is UHMW polyhydrocarbon.

25. The in vivo implant of claim 24, wherein the in vivo implant increases in its degree of crystallinity by about 1% if annealed.

26. The in vivo implant of claim 23, wherein the free radical generating chemical is selected from the group consisting of: peroxides, peresters, azo compounds, disulfides, dimethacrylates, tetrazenes, and divinyl benzene.

27. The in vivo implant of claim 26, wherein the polymer is chemically crosslinked by a free radical generating chemical, and the polymer is UHMW polyhydrocarbon.

28. The in vivo implant of claim 17, capable of suffering less than or equal to one-fifth of the wear suffered by another in vivo implant made from an uncrosslinked polymer.

29. The in vivo implant of claim 28, wherein the polymer is chemically crosslinked by a free radical generating chemical, and the polymer is UHMW polyhydrocarbon.

30. A polyhydrocarbon capable of maintaining a degree of crystallinity of about 42% or less after gamma irradiation to an average dose of about 3.4 Mrad or less.

31. The polyhydrocarbon of claim 30, wherein the polyhydrocarbon has a crystallinity of about 39.8% or less before the gamma irradiation.

32. The polyhydrocarbon of claim 30, wherein the polyhydrocarbon is UHMW polyhydrocarbon.

33. A crosslinked in vivo implant comprising a component of an animal joint, said in vivo implant being capable of suffering about one-fifth or less of the wear suffered by an uncrosslinked in vivo implant, wherein the crosslinked in vivo implant and the uncrosslinked in vivo implant are made of UHMW polyethylene and have been sterilized by irradiation, and the crosslink is achieved by a method selected from the group consisting of:



FIG. 1A

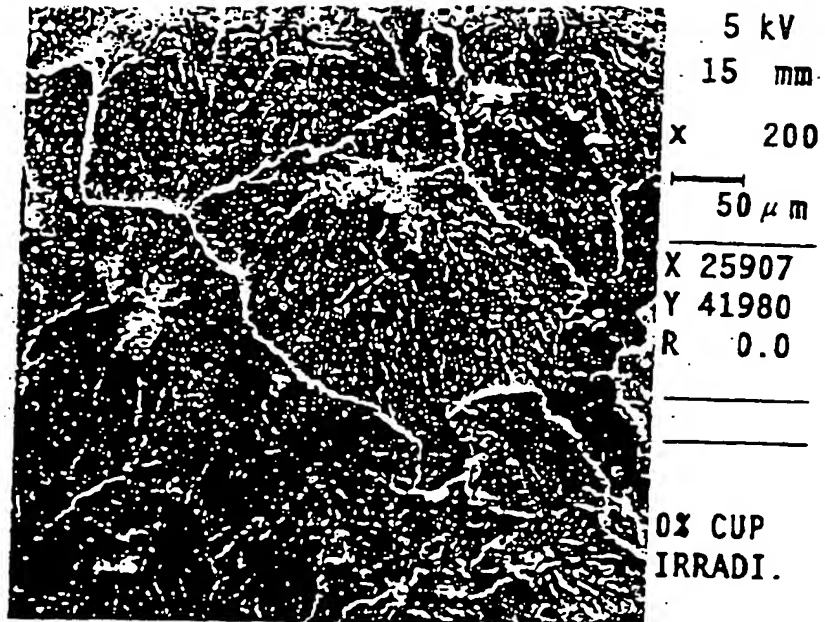


FIG. 1B

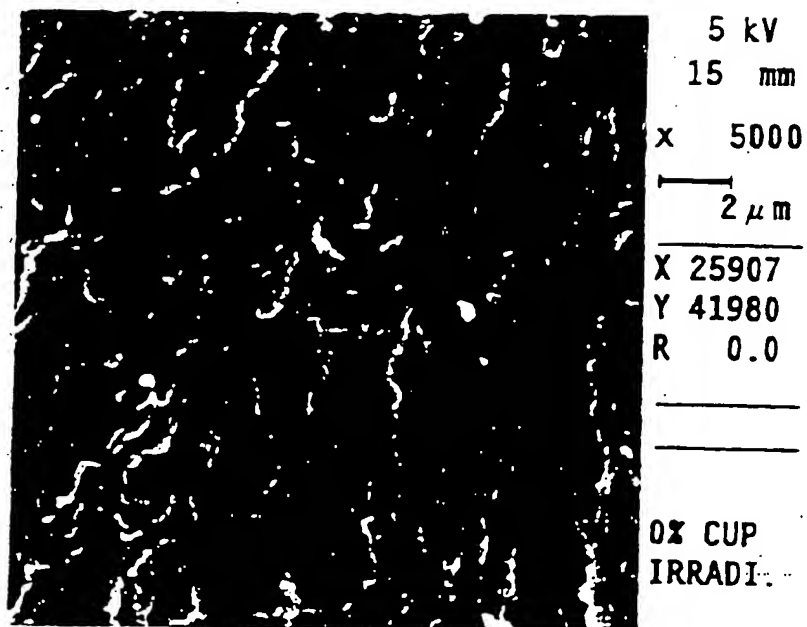


FIG. 2A

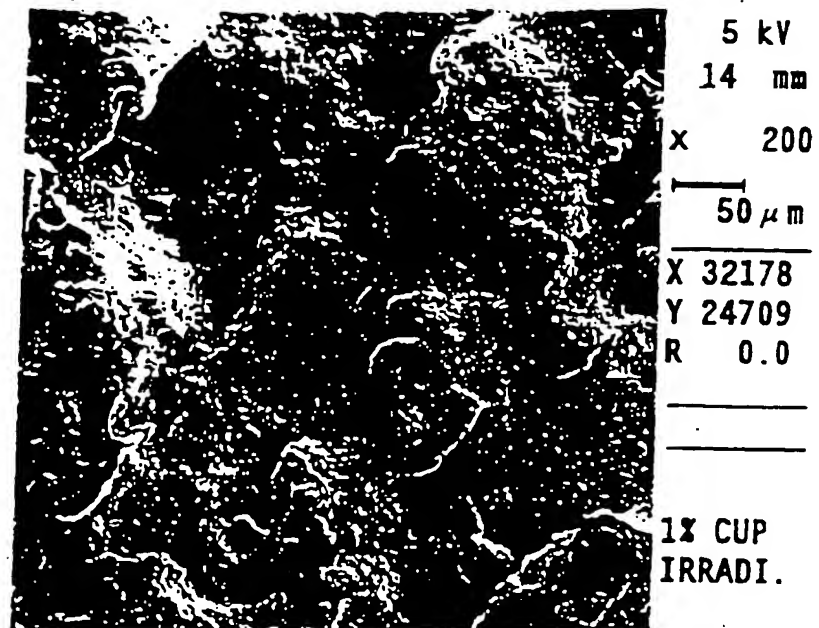


FIG. 2B

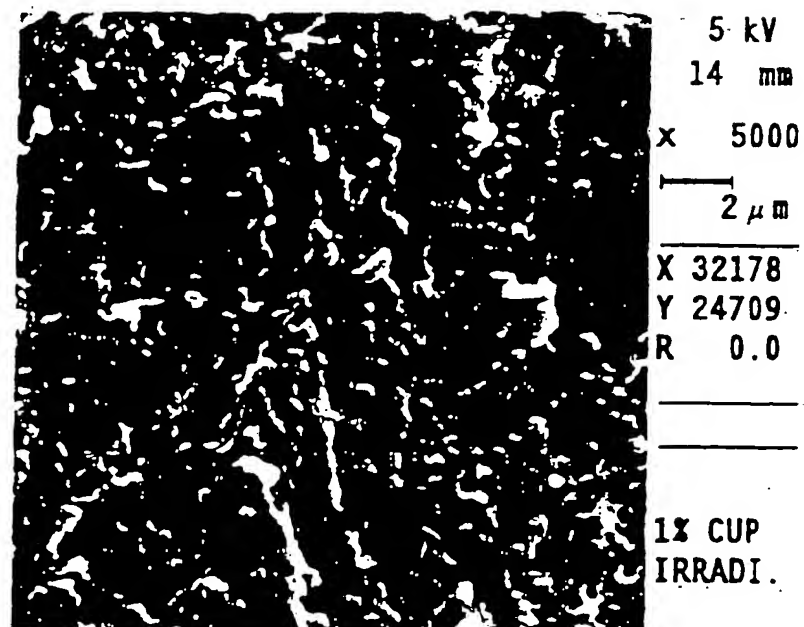


FIG. 3A

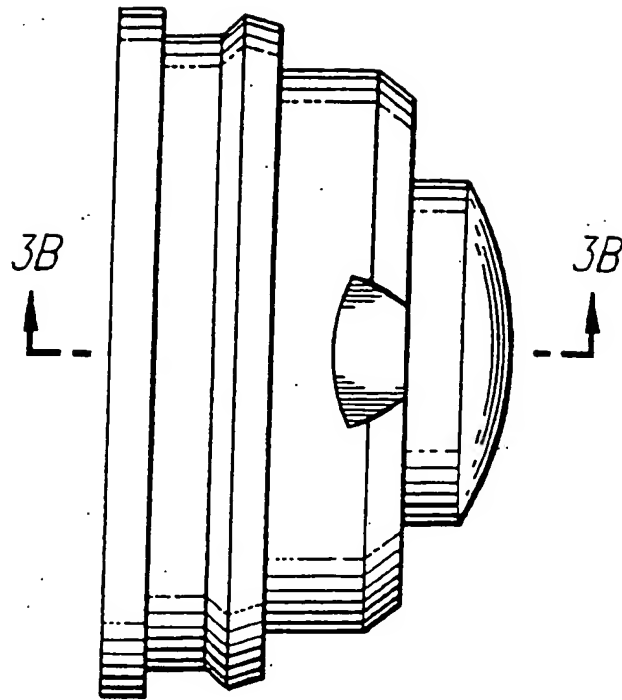


FIG. 3B

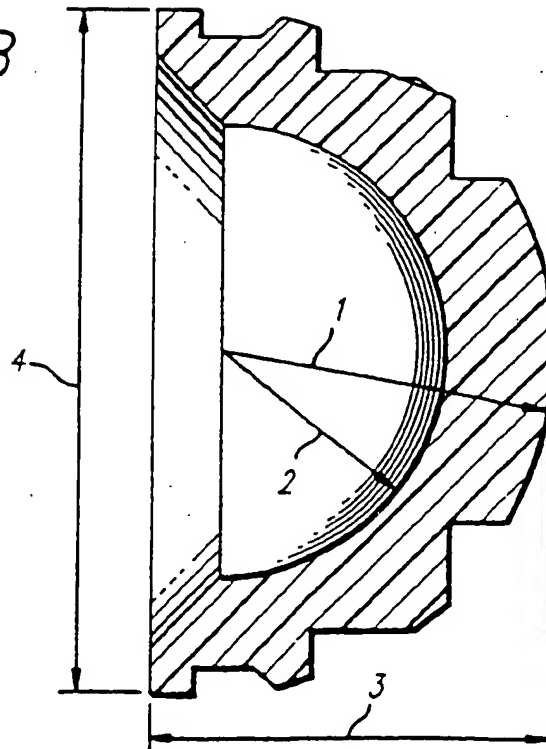


FIG. 4

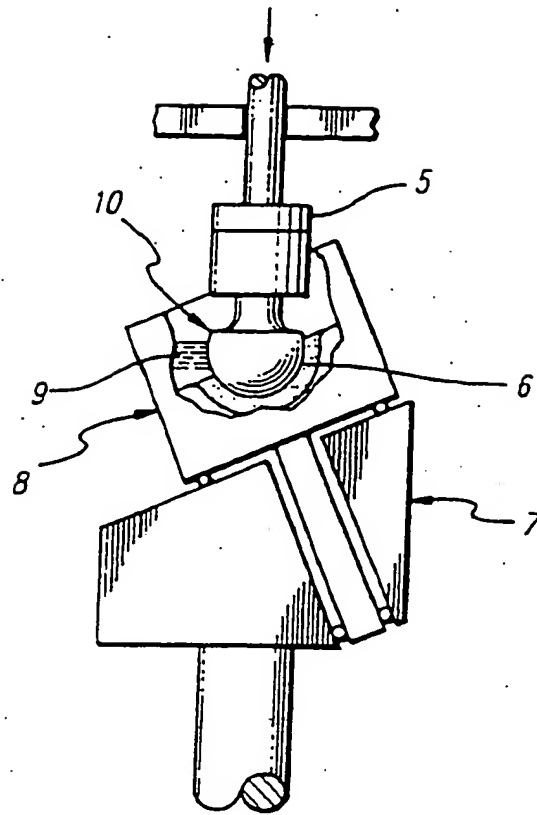
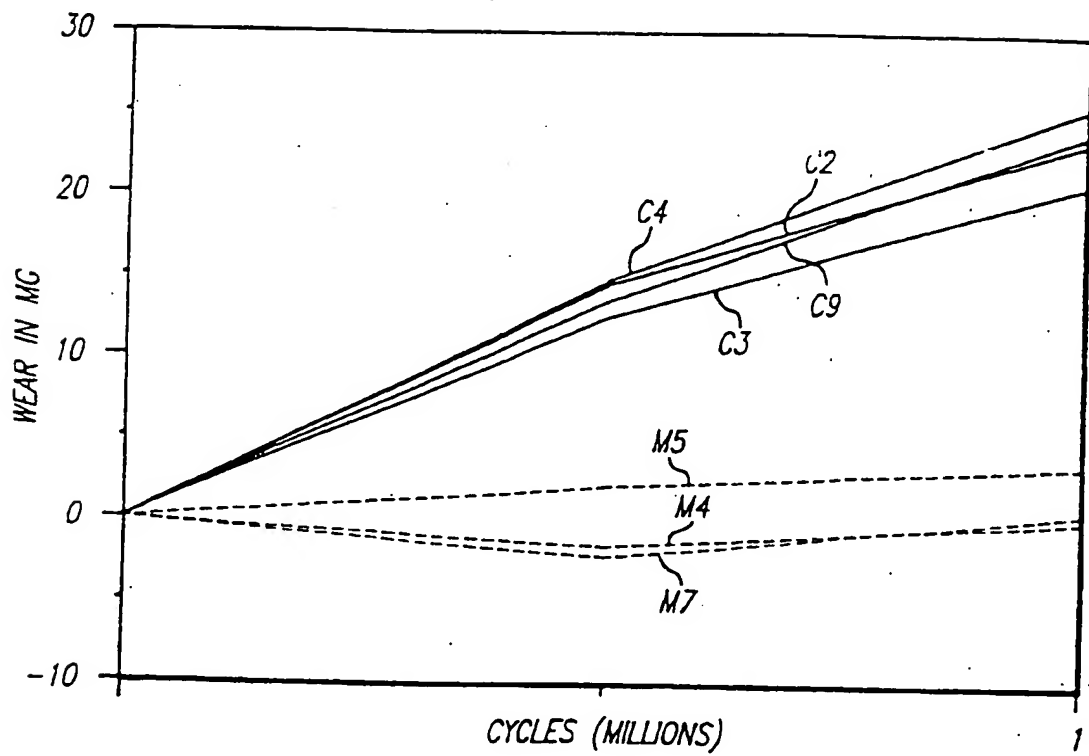


FIG. 5





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 96 30 0113

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
D, X	POLYMER, vol. 30, no. 5, May 1989, GB, pages 866-873, XP000569234 DIJKSTRA D.J. ET AL: "Cross-linking of ultra-high molecular weight polyethylene in the melt by means of electron beam irradiation" *abstract* * page 866, left-hand column, paragraph 2 * * figure 5; table 1 *	1	C08J3/24 C08J3/28 A61F2/30 //C08L23:06
X	BE-A-1 001 574 (FLATECH INTERNATIONAL) 5 December 1989 * claims 1,3 * * page 5, line 13 - line 16 * * page 8, line 17 - line 19 *	8-11	
D, A	POLYMER, vol. 23, no. 09, August 1982, GB, pages 1944-1952, XP000569235 DE BOER J. ET AL: "Cross-linking of ultra-high molecular weight polyethylene in the melt by means..." *abstract* * figure 1; table 1 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 6) C08J A61F
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 87-338571[48] XP002001745 & JP-A-62 243 634 (NIPPON OIL KK) , 24 January 1987 * abstract *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 April 1996	Examiner Niaounakis, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			